

Different scenarios of the late stages of condensation

Victor Kurasov

Abstract

The late stages of the nucleation have been described analytically. The approximate solution of the Zel'dowich-Folmer-Frenkel equation has been constructed.

Introduction

The process of the evolution after the end of nucleation (the main stage) and the consumption of the main quantity of the surplus metastable phase requires a separate description. This description can be based on the real form of the size spectrum [5] or can be done by the asymptotic analysis [1], [2].

The regime will be chosen as the free molecular one. This is done because the formation of the exhausted zones around the droplets strongly influences the kinetics and the description can not be based on the averaged characteristics. The only situation where the diffusion regime can be combined with the averaged characteristics is when the embryos go from one cave to another and change many exhausted zones. But this situation can be reduced to the effective absence of the cave and, thus, the regime will be the free-molecular one. It is important because earlier there was the restriction that the size is less than the length of the free motion of a molecule divided by the coefficient of condensation. Now this restriction is not essential.

The first stages of the late evolution were investigated in [5].

1 Balance equation

Define n as the number of embryos with ν molecules. The evolution in time t is described by equation

$$\frac{\partial n}{\partial t} = W^+(\nu - 1)n(\nu - 1) - W^-(\nu)n(\nu) - W^+(\nu)n(\nu) + W^-(\nu + 1)n(\nu + 1)$$

Here W^+ is the direct kinetic coefficient, W^- is the inverse kinetic coefficient. In the Fokker-Planck approximation there will be a diffusion and the regular growth.

In approximation of the pure diffusion the balance equation will be

$$\frac{\partial n}{\partial t} = W^+(\nu)[n(\nu - 1) - n(\nu) - n(\nu) + n(\nu + 1)]$$

and

$$\frac{\partial n}{\partial t} = W^+(\nu)\frac{\partial^2 n(\nu)}{\partial \nu^2}$$

2 Some estimates

According to [5] after the regular relaxation there will be a diffusion erosion of the spectrum. For this stage one can give some estimates.

2.1 Diffusion

One has to use s -scale. Here s is the surface of the embryo

$$s = \nu^{2/3}$$

This is because the kinetic coefficient of absorption W^+ is proportional to s

$$W^+ = W^0 s$$

Then in diffusion equation will be

$$\frac{\partial n}{\partial t} = W^0 \nu^{2/3} \frac{\partial^2 n(\nu)}{\partial \nu^2} \tag{1}$$

In the leading term

$$\frac{\partial^2 n(\nu)}{\partial \nu^2} \rightarrow \nu^{-2/3} \frac{\partial^2 n(\nu)}{\partial s^2}$$

Then

$$\frac{\partial n(\nu)}{\partial t} = W^0 \frac{\partial^2 n(\nu)}{\partial s^2}$$

The same will be for $n(s)$.

The diffusion scale will be

$$s_{diff} = t^{1/2}$$

For the linear size of an embryo

$$\rho = \nu^{1/3}$$

we have

$$\rho_{diff} \sim t^{1/4}$$

2.2 Regular growth

The coordinate of the regular growth will be determined from

$$\frac{d\rho}{dt} = \frac{\zeta}{t_t}$$

Here t_t is the characteristic time, ζ is the supersaturation defined by

$$\zeta = n_1/n_\infty - 1$$

where n_1 is the molecules number density of vapor, n_∞ is the molecules number density of the saturated vapor.

Then

$$\rho_{reg} = \int \frac{\zeta}{t_t} dt$$

The behavior of ζ is given by

$$\zeta = \frac{2a}{3\rho_c}$$

where index c marks the critical embryo.

Having taken

$$\rho_c \sim \rho_{diff}$$

we get

$$\zeta \sim \frac{2a}{3\rho_c} \Big|_{\rho_c=\rho_{diff}}$$

Then

$$\zeta \sim \frac{2a}{3\rho_c} \Big|_{\rho_c=t^{1/4}}$$

and

$$\zeta \sim t^{-1/4}$$

Then

$$\rho_{reg} \sim t^{3/4}$$

We see that

$$\rho_{diff} \ll \rho_{reg}$$

and it is clear that the main quantity of substance will be in the tail growing regularly.

Approximately we assume that at the period when the tail will be essential the following approximation $W^0 \approx const$ takes place.

3 The form of the tail

We determine the form of the tail. Imagine that at big sizes there is a dominating regular growth, at small sizes of the critical order there is a dominating diffusion. The boundary will be marked by the index b .

Certainly, at the very small sizes there is a regular dissolution. But this region is simply negligible and can be expelled by the transition of a zero point.

Then for $\rho > \rho_b$

$$\rho - \rho_b = \int_{t'}^t \frac{\zeta}{t_t} dt$$

Then the distribution function f is given by

$$f(\rho, t) = f_b(\rho_b, t')$$

To get f_b one can use the diffusion approximation according to [7], [5]

$$f_b = \frac{A_0}{\sqrt{4W^0 t'}} \exp\left(-\frac{(s_b - s_c)^2}{4W^0 t'}\right)$$

In the absolutely stationary approximation one can put the normalizing constant

$$A_0 = 1$$

Due to the dissolution this constant will be another and this question will be solved later.

Now we consider

$$\frac{(s_b - s_c)^2}{4W^0 t'}$$

As an estimate one can take

$$\rho_b - \rho_c = 2\rho_c$$

Then

$$\frac{(s_b - s_c)^2}{4W^0 t'} \sim \frac{64\rho_c^4}{4W^0 t'}$$

If we take $\rho_c \sim t^{1/4}$ (more precise it is necessary to take $\rho_c \sim W^0 t^{1/4}$) then

$$\frac{(s_b - s_c)^2}{4W^0 t'} \sim \frac{64}{4}$$

Then

$$f_b \sim \frac{A_0}{\sqrt{4W^0 t'}} \exp(-16)$$

4 More precise formula

One can use another more precise equation (see [7], [5])

$$f_b = \frac{A_0}{\sqrt{4W^0 t}} \exp\left(-\frac{(s - s_{c0})^2}{4W^0 t}\right) - \frac{A_0}{\sqrt{4W^0 t}} \exp\left(-\frac{(s + s_{c0})^2}{4W^0 t}\right)$$

Here s_{c0} marks the initial position of a critical surface.

After the transformations we get

$$f = \frac{A_0}{\sqrt{4W^0 t}} \exp\left(-\frac{s^2}{4W^0 t}\right) \exp\left(-\frac{s_{c0}^2}{4W^0 t}\right) \left[\exp\left(\frac{2ss_{c0}}{4W^0 t}\right) - \exp\left(-\frac{2ss_{c0}}{4W^0 t}\right)\right]$$

One can see that

$$ss_{c0}/4W^0 t \ll 1$$

Really, since

$$s^2 \sim 4W^0 t$$

and s_{c0} is fixed we come to

$$ss_{c0}/4W^0 t \sim t^{-1/2} \ll 1$$

Then after the decompositions of the corresponding exponents one can come to

$$f = \frac{A_0}{\sqrt{4W^0t}} \exp\left(-\frac{s^2}{4W^0t}\right) \exp\left(-\frac{s_{c0}^2}{4W^0t}\right) \frac{4ss_{c0}}{4W^0t}$$

So,

$$f \sim y \exp(-y^2)$$

with

$$y = \frac{s}{\sqrt{4W^0t}}$$

The maximum of this distribution is attained at

$$y_m = \sqrt{2}/2$$

This value will be close to the critical value

$$y_m \sim y_c$$

For

$$y_b = \alpha y_c$$

with some parameter α we get

$$f_b = \frac{A_0}{\sqrt{4W^0t}} \exp(-\beta)$$

with constant β .

5 Dissolution of the spectrum head

The dissolution of the head determines the form of the tail.

At first there is a pure dissolution of a gaussian and

$$\rho_c \approx const$$

Then

$$f_b \sim \frac{1}{\sqrt{4W^0t}} \exp(-(s_b - s_c)^2/(4W^0t))$$

or

$$f_b \sim \frac{1}{\sqrt{4W^0t}} \exp(-9W^0\rho_{c0}^4/(4W^0t))$$

For the behavior of f_b we get

$$f_b \sim \frac{1}{t^{1/2}} \exp(-\gamma/t)$$

with a positive parameter $\gamma = \text{const.}$

The last function is positive, it has an evident asymptotic behavior $f_b \rightarrow t^{-1/2}$ at big t . At small t it goes to zero. Thus, it has a maximum.

To see the formation of the tail one can approximately write

$$\rho - \rho_{c0} = \frac{\zeta_0}{t_t}(t - t')$$

where ζ_0 is some initial supersaturation. Here we assume ζ_0 to be a constant which is a very strong assumption. So, below all results will have the power of estimates.

The maximal size ρ_{lim} is

$$\rho_{lim} = \rho_{c0} + \zeta_0 t/t_t$$

Then having put the starting moment at zero one can get

$$t' = (\rho - \rho_{lim})t_t/\zeta_0$$

The distribution at the tail looks like

$$\tilde{f}_\rho = f(z) = \left(\frac{\zeta_0}{zt_t}\right)^{1/2} \exp\left(-\frac{\gamma\zeta_0}{zt_t}\right)$$

as a function of

$$z = \rho_{lim} - \rho$$

Now we shall calculate the quantity of substance in the tail G_{tail} . We get

$$G_{tail} = \int_{\rho_{c0}}^{\rho_{lim}} \rho^3 \left(\frac{\zeta_0}{t_t(\rho_{lim} - \rho)}\right)^{1/2} \exp\left(-\gamma \frac{\zeta_0}{t_t(\rho_{lim} - \rho)}\right) d\rho$$

Having introduced

$$y = \frac{\rho_{lim} - \rho}{\epsilon} \quad \epsilon = \gamma\zeta_0/t_t$$

we get

$$G_{tail} = \frac{\epsilon}{\gamma^{1/2}} \int_0^{\frac{\rho_{lim} - \rho_{c0}}{t_t}} (\rho_{lim} - \epsilon y)^3 \frac{1}{y^{1/2}} \exp(-1/y) dy$$

One can see that G_{tail} grows very fast. The asymptotics is

$$G_{tail} \rightarrow \rho_{lim}^{5/2} \sim t^{5/2}$$

But this behavior will take place only until

$$ss_c \sim 4W^0t$$

After this moment of time the boundary condition will be another

$$f|_{\rho_b} = A_0 \exp(-const)$$

or at larger scales of time

$$f|_{\rho_b} \sim t^{-1/2}$$

Alternative approach

At the further stage

$$f|_{\rho_b} \sim \frac{1}{\sqrt{t}}$$

So, we see that the variation is very small. The drift of ρ is rather small also

$$\rho \sim \int \zeta dt \sim t^{3/4}$$

because of

$$s_c \sim t^{1/2} \quad \rho_c \sim t^{1/4} \quad \zeta \sim t^{-1/4}$$

The subintegral function g_{tail} in the quantity of substance

$$G_{tail} = \int g_{tail} d\rho$$

in the tail grows like

$$g_{tail} \sim t^{9/4}$$

It grows fast.

6 Impulse regime

Since G_{tail} grows very fast one has to analyze this behavior.

At first

$$G_{tail} \ll G_{total} \quad (2)$$

where G_{total} is the total quantity of substance in droplets.

The main role here is played by diffusion and the solution can be described with the help of combinations of Gaussians. This model will be called as the diffusion-regular model. It is investigated in [5].

Since g_{tail} grows fast it means that the monodisperse approximation for G_{tail} is quite suitable

$$G_{tail} \sim \rho_{eff} N_{eff}$$

Here N_{eff} is the effective number of droplets in the tail and ρ_{eff} is their coordinate. Certainly, N_{eff} is not a constant value, it grows.

At t determined by

$$G_{tail} \sim G_{total} - G_{tail}$$

the tail begins to eat the head of the spectrum. Here the tail is non-essentially decreasing one. It occurs very fast and the spectrum eats at first the head and then it begins to eat the rather flat beginning of the tail.

This process can be easily described by the regular growth of the tail and by the regular dissolution of the eaten part of the spectrum.

Then only the end of the tail will exist. This end can be then treated as a monodisperse spectrum. Later this part will be dissolved by diffusion and the process repeats.

We shall call this process as the "impulse condensation".

This part is described in [5].

7 Short tail

A question whether the process of impulse condensation repeats arises here. From the first point of view it seems that this process will infinitely repeat. But there is one objection.

The function $f(t) = \exp(-\gamma/t)/\sqrt{t}$ described above has a maximum. This maximum takes place at $t/\gamma \equiv y = y_m \approx 2$ and for y essentially less than y_m there is a rapid decrease to zero.

Certainly, after every cycle the time t has to be shifted.

The crucial point is whether at y_m the condition (2) is observed. An alternative case

$$G_{tail} \sim G_{total} - G_{tail}$$

at y_m leads to another further evolution. Here the tail is essentially decreasing. This case will be called as "the case of adjusted tail".

In this section one can study the evolution on the base of the regular growth. This radically simplifies the situation.

Here we shall give the main ideas of description in this situation. The vapor consumption by the head of the tail can eat only the same head of the tail. There is no other parts to eat. Then we come to the following balanced picture:

- The task is to determine $\rho_b = 2 \div 3\rho_c$, $\rho_c = 2a/3 \ln(\zeta + 1) \approx 2a/3\zeta$ where a is a renormalized surface tension.
- The size distribution for $\rho > \rho_b$ is known. We have

$$f(\rho, t) = f(x)$$

for

$$x = z - \rho$$

$z \equiv \rho_{lim}(t)$. Then

$$G_{tail} = \int_0^{z-\rho_b} (z-x)^3 f(x) dx$$

- For $f(x)$ we have

$$f(x) \sim \exp(-\frac{\tilde{\gamma}}{x})/\sqrt{x}$$

- The balance equation is

$$G_{tail} + G_{head} + n_\infty(\zeta + 1) = const$$

where G_{head} is the quantity of the substance in a region $0.7\rho_c < \rho < \rho_b$. In the region $\rho < 0.7\rho_c$ one can simply neglect the substance.

- In the region $0.7\rho_c < \rho < \rho_b$ one can write the pure¹ diffusion equation (1) with boundary conditions

$$f(\rho, t) = 0$$

¹I.e. without the regular growth and with the constant coefficient of diffusion.

at $\rho = 0.7\rho_c$

$$f(\rho, t) = f_{tail}(x)$$

at $\rho = \rho_b$

- In the region $\rho < 0.7\rho_c$ one can simply neglect the evolution.

8 Further simplification

Already the last system of equations can be solved when we know $f(x)$. The function $f(x)$ has to be known from the initial conditions. These conditions are:

- The direct result of the nucleation period [4].
- The result of the impulse regime [5].

To show the result in a most simple way one can use some simplifications. Further simplification is the following

- To write the balance equation as

$$G_{tail} = fixed$$

- To use that

$$G_{tail} \sim N_{tail}\rho_b$$

where N_{tail} is the effective (proportional) number of the droplets in the tail.

The function f_{tail} is one of the possible realizations, which has a certain disadvantage. Really, for $\rho > \rho_{lim}$ the distribution is zero. Meanwhile, the diffusion in the region $\rho > \rho_b$ inevitably leads to the big droplets. Assume that the behavior of the gaussian at big arguments can be approximated as

$$\tilde{f} \sim \exp(-\gamma'\rho)$$

with some parameter γ' .

The same asymptotic can be derived from f_{tail} by the steepest descent method.

So, the last approximation is very fruitful. It allows to calculate the integrals for G_{tail} analytically.

One can make some new simplification. Since the spectrum is rather sharp, it means that

$$\frac{d\rho_b}{dt} \sim \frac{d\rho_c}{dt}$$

which leads asymptotically to

$$\zeta \sim t^{-1/2}$$

$$\rho \sim t^{1/2}$$

Since the diffusion width is $s_d \sim t^{1/2}$, $\rho_d \sim t^{1/4}$ we see that the diffusion does not radically change the character of the process. However, since the Gaussian does not have a finite support the droplets with the greatest sizes which will be the main in further consumption appears due to diffusion. This is one more point for the approximation \tilde{f} .

The constant γ is not a precise constant but a slowly varying function. This effect can be taken into account by standard methods.

An approximation \tilde{f} is so simple that we have no need to use the monodisperse approximation. One can calculate G_{tail} directly by integration

$$G_{tail} \sim \int_{\rho_b}^{\infty} (z - x)^3 \exp(-\gamma' x) dx$$

and the integral can be taken analytically.

9 Initial asymptotic solution

Since we came to the balance equations typical for the asymptotic solutions of Lifshic and Slyozov [1] it is necessary to analyze this approach.

As a regular law of droplets growth one has to take the precise expression

$$\frac{d\rho}{dt} = \frac{6\sigma}{9t_t} \left(\frac{1}{\rho_c} - \frac{1}{\rho} \right)$$

where σ is the renormalized surface tension.

For

$$u = \rho/\rho_c$$

one gets

$$\frac{du}{dt} = \frac{6\sigma}{9t_t\rho_c} \left(\frac{1}{\rho_c} - \frac{1}{\rho} \right) - \frac{u}{\rho_c} \frac{d\rho_c}{dt}$$

In the reduced coordinates

$$\frac{du}{d\tau} = (1 - 1/u) - \tilde{\gamma}u$$

$$\tilde{\gamma} = \rho_c \frac{d\rho_c}{dt}$$

Then to escape the violence of the substance balance one has to observe

$$\frac{du}{dt} \leq 0$$

for all u .

The last relation will take place for every time τ increasing in time since

$$\frac{du}{d\tau} = \frac{du}{dt} \frac{dt}{d\tau}$$

Namely

$$\tau = 3 \ln(\rho_c / \rho_c(t=0))$$

was chosen by Lifshic, Slyozov (LS).

The last requirement is very strong. In reality, one can imagine the situation where this requirement is not valid. In the general case it is necessary that this requirement takes place only in the integral sense. But in LS theory this requirement has to be valid at every moment.

LS required that

$$\max_{\{u\}} \left(\frac{du}{d\tau} \right) \equiv r \rightarrow 0$$

Meanwhile the real condition should be the following:

- If r has a power asymptotics (asymptotics as an argument in some power) then this asymptotics has to be zero

But the situation when r has no asymptotics is also quite possible. For example, the case of oscillations drops out of attention here.

The crucial supposition of LS theory is the existence of the asymptotics for r (in the class of constants).

The recipe of LS is to consider r as the monotonous function and then it is reasonable to put $r = 0$ asymptotically.

It is necessary to stress that the condition $du/dt \leq 0$ for every u leads to

$$\frac{d\rho}{dt} - \frac{\rho}{\rho_c} \frac{d\rho}{dt} \leq 0$$

for every ρ or

$$\frac{d \ln \rho}{dt} \leq \frac{d \ln \rho_c}{dt}$$

for every ρ . This is very important relation.

From the last inequality it follows that every ρ can not escape and will inevitably be dissolved. But at some u there will be no dissolution. Let it be u_0 . Requirement $r = 0$ leads to

$$u_0 = 2$$

$$\frac{\frac{6\sigma}{9t_t}}{\rho_c^2 \frac{d\rho_c}{dt}} = 4$$

The last equation can be easily integrated which leads to

$$-4\rho_c^{-1} = const + t \frac{6\sigma}{9t_t} \quad (3)$$

but one has to note that if we observe the validity of the previous equation only in the averaged sense we get approximately the same integral law. So, one can not regard the law of 4/9 (this is the characteristic coefficient in the diffusion case, here the regime is the free-molecular one) as an experimental justification of LS approach.

The law (3) can be easily justified. Really, if there will be another power asymptotic then immediately we come to the violence of the balance condition.

One has also to stress that it is absolutely impossible to differentiate (3), the result will have nothing in common with a real situation. This fact is typical for such asymptotics.

10 The form of the spectrum in LS theory

It is clear that the evolution of the system is governed by the spectrum of the droplets sizes. This function determines the behavior of the supersaturation in the system.

In frames of LS approach the behavior of ρ_c is already known. Then it is possible to solve the inverse problem: to reconstruct the spectrum on the base of the behavior of supersaturation. The sense of this way of derivation is wrong, but technically it is quite possible.

Under the regular law of growth one can find for the distribution function

$$\phi(\tau, u) = -\xi(\tau - \tau(u))/v_u$$

where

$$v_u = du/d\tau$$

is already known and

$$\tau(u) = \int_0^u du/v_u$$

is also known and ξ is some arbitrary function which is going to be determined. The balance equation allows to determine the form of ξ which solves the problem.

To solve it in the simple form τ is chosen as

$$\tau = 3 \ln(\rho_c(t)/\rho_c(t=0))$$

. Then the balance equation in a closed system will be

$$\exp(\tau) \int_0^u u^3 \phi(\tau, u) du = 1$$

which can take place only if

$$\xi(\dots) = \exp(\dots)$$

The spectrum is zero for $u > u_0$ and continuously goes to zero for $u \rightarrow u_0 - 0$. So, the essential part of the spectrum ill be dissolved at finite times τ and t . Here it is necessary to stress that now it is clear that the deviation of r from zero at some finite interval (it is quite possible) can lead to the absolutely another form of the spectrum. So, the form of the spectrum is determined only with the help of the strong supposition of LS theory about the behavior of the critical size, i.e. about the supersaturation.

11 Correction for γ

The limit value $r \equiv 0$ is not acceptable even in LS theory. The next step leads to correction of r . Ordinary, the correction is many times greater then the precedent value of r which allows Osipov and Kukushkin [2] to speak about the non-uniform character of LS decompositions.

In frames of LS theory it is possible to write a correction term and to fulfill the next step of calculations. Osipov and Kukushkin (OK) [2] follow another way. Certainly, since the result in the first approximation is known it is possible to rewrite the formulas in such a way that γ will be zero and the first approximation has to inevitably include the correction term in LS approach. Since the conclusions of OK theory are important it is necessary to consider it. We omit all details which can be found² in [2].

Having introduced

$$\tau = \frac{1}{4} \int_0^t \rho_c^{-2} dt$$

and redefined $u = \rho/2\rho_c$ one can come to

$$\frac{du}{d\tau} = \frac{(u-1)^2}{u} + \gamma u$$

Now the condition $r = 0$ corresponds to $\gamma = 0$ and every correction for γ will be giant in comparison with $\gamma_0 = 0$. Then the asymptotics here has to include the correction term already in the main order.

The approach with correction gives

$$\gamma = 1/(4\tau^2)$$

The substitution

$$v = (1-u)^{-1} - \ln|u-1|$$

brings the rate of growth to

$$\frac{dv}{dt} = 1 + \gamma(1+\psi)^2$$

where ψ satisfies

$$\psi + \ln|\psi| = v$$

²The initial total number of embryos is found with an error from [3] because the asymptotic analysis [3] is not valid, it is necessary to use [4].

and asymptotically

$$\frac{dv}{dt} = 1 + \gamma v^2$$

The initial asymptotics in LS theory corresponds to $\gamma = 0$ and then asymptotically

$$v = \tau + \text{const}$$

The initial asymptotics in OK theory corresponds to $\gamma = 1/(4\tau^2)$. Then asymptotically

$$v \rightarrow 2\tau$$

12 Correction for the distributions

The distribution function can be in frames of LS and OK theories found from

$$f(u, \tau) = \xi(C(u, \gamma)) \frac{\partial C}{\partial u}$$

where C is the integral of the law of growth.

Concrete calculations will give the following results

- In LS theory

$$v - \tau = \text{const}$$

or

$$\exp(v - \tau) = \text{const}$$

i.e.

$$C_{LS} = \frac{1}{1-u} \exp\left(-\frac{1}{1-u} - \tau\right)$$

is the integral of evolution Then ξ is

$$\xi \sim C_{LS}^2 \text{ at } C_{LS} > 0, \quad \xi \sim 0 \text{ at } C_{LS} < 0$$

Then the spectrum is

$$\phi_{LS} = \frac{2u}{(1-u)^4} \exp\left(-\frac{2u}{1-u}\right)$$

- In OK theory

$$v - 2\tau = \text{const}$$

or

$$\exp(v - 2\tau) = \text{const}$$

i.e.

$$C_{OK} = \frac{1}{1-u} \exp\left(-\frac{1}{1-u} - 2\tau\right)$$

is the integral of evolution Then ξ is

$$\xi \sim C_{OK} \text{ at } C_{OK} > 0, \quad \xi \sim 0 \text{ at } C_{OK} < 0$$

Then the spectrum is

$$\phi_{OK} = \frac{u}{(1-u)^3} \exp\left(-\frac{u}{1-u}\right)$$

and it essentially differs from LS theory.

13 Further corrections

The essential difference of spectrums is the striking feature of the LS theory. But it is rather easy to see that such a feature will be natural for all further corrections.

Suppose that the integral of evolution at the previous step is established. Then we can reformulate the rate of growth as

$$\frac{du}{dt} = F(u) - \gamma u$$

where F is a known function.

Here we use for simplicity t instead of τ .

In the zero approximation (LS theory)

$$F \sim -u^{-1} + 1/2$$

in the first approximation³ (OK theory)

$$F = (u - 1)^2/u$$

³With a renormalization

etc.

Let w be the solution of the equation with $\gamma = 0$, i.e.

$$\int \frac{du}{F(u)} = t + \text{const}$$

Then at the previous step

$$\frac{dw}{dt} = 1$$

At the current step

$$\frac{dw}{dt} = 1 + \gamma u(w)$$

So, w is a straight analog of v .

There can be two situations:

1. Asymptotically $w \rightarrow t$.
2. Asymptotically $w \rightarrow l(t) \neq t$.

In the first situation the spectrum remains absolutely the previous one. There is absolutely no corrections.

In the second situation the correction is essential. Instead of $w - t$ as the integral of evolution one has to use $w - l(t)$. It means that instead of w one has to use $l^{\{-1\}}(w)$ where $l^{\{-1\}}$ is the inverse function.

The difference in spectrums is striking.

So, the alternative is to have no corrections or the striking corrections. This is the consequence of the use of Lifshic-Slezov variables and a certain disadvantage of LS and OK approaches.

14 Application of asymptotics

The ideology of LS and OK asymptotic analysis is one and the same:

- The asymptotic of some given function of the supersaturation in the class of powers is prescribed.
- The balance condition at asymptotics leads to the determination of the supersaturation as the function of time.

- The form of the size spectrum is reconstructed on the base of the given supersaturation.

Meanwhile, under the regular growth of the embryos the natural sequence of actions is the following

- The size spectrum is given from initial conditions
- The dissolution of the size spectrum together with the balance equation determines the behavior of the supersaturation
- The tail of the spectrum at big sizes determines the asymptotics of the supersaturation and of coefficients in the regular law of the droplets motion.

We see that from the last point of view the LS and OK theories are inconsistent. Then why they correspond to the asymptotic behavior found from experiment?

At first one has to mention that the accuracy of experimental measurements is not high: even the striking difference between LS and OK drops out of experiments. Hence, we have to conclude that the experiment gives only the approximate form of the size spectrum with maximum and two different rather short wings.

Now we shall see that the form of the size spectrum obtained in LS and OK theories is rather typical at least approximately.

The tail of the Gaussian can well approximated by

$$\xi_{as} = \exp(-const * \rho)$$

with some constant *const*. We shall call this constant Λ and suppose it to be a slow function of ρ to have

$$\Lambda(\rho + \Lambda^{-1}) - \Lambda(\rho) \ll \Lambda(\rho)$$

Then the exponential approximation will be valid at least at the essential part of the size spectrum.

These transformations are absolutely adequate to the standard approach of the steepest descent method.

The same approximation can be established in u -scale. The constant can simply cancelled by renormalization. Then

$$\xi_{as} \sim \exp(-u)$$

Now we shall approximate $\tau(u)$ for two values u_1 and u_2 at the essential part of the size spectrum. The simplest approximation is the following

$$\tau(u_1) - \tau(u_2) = \frac{d\tau(u)}{du}(u_1 - u_2)$$

which is the linear connection. Then the exponential form of the spectrum over $\tau(u)$ will be conserved

$$\xi_{as} \sim \exp(-\tau(u))$$

Since ξ has to be the function of $\tau - \tau(u)$ we come to

$$\xi = \exp(\tau - \tau(u))$$

which lies in the base of LS and OK reconstruction of the size spectrum.

To get the spectrum one has to divide ξ on v_u . The last value is determined by the regular law of growth. Certainly, one can not guarantee that the parameter γ corresponds to $r = 0$. When it really corresponds to $r = 0$ there will be LS asymptotic. When γ corresponds to some small r less than zero then there will be an extremum associated with the minimum of v_u .

One can see that since r is rather small in the absolute value there is a maximum of ϕ near u_0 . One has to note that in the experiment there is no evident way to determine the critical size. Then there is no way to determine the position of the size spectrum, but only its form.

Since Λ is not a true constant one can say about the quasistationary solution with a smooth variation of parameters and a form of the spectrum.

These considerations evoke the ideas associated with the square approximation of the rate of growth $du/d\tau$ near the maximum which were presented in [6].

15 Direct determination of γ .

Although the precise asymptotic can not be directly used to determine the evolution of the system one can suggest another approach.

Now we return to the description of the evolution.

The rate of growth can be written as

$$\frac{du}{d\tau} = \hat{F}(u, \gamma(\tau))$$

The integration of this equation gives $\tilde{\tau}(u)$. Symbolically this can be written as

$$\tilde{\tau}(u) = \int \frac{du}{v_u}$$

where

$$v_u = \frac{du}{d\tau}$$

The problem of integration of the rate of growth is very important and analytically it is difficult to do, but here we suppose that it is fulfilled.

The balance equation has to be written as

$$G_{total} = const$$

It is possible to neglect the surface mother phase. It can be reduced to

$$\exp(\tau) \int_0^{u_{lim}} u^3 \phi(u, \tau) du = const$$

where ϕ is the distribution function, u_{lim} is the maximal size.

The regular law of growth leads to

$$\phi(u, \tau) = \frac{\xi(\tau - \tilde{\tau}(u))}{-v_u}$$

Then the balance equation will be

$$\exp(\tau) \int_0^{u_{lim}} \frac{u^3 \xi(\tau - \tilde{\tau}(u))}{-v_u} du = const$$

But the last equation is not an equation on the function ξ as in the LS and OK theories but an equation on $\tilde{\gamma}$. The function ξ is known from the initial conditions for this equation. This is the crucial difference between our theory and LS or OK theory. The dependence $\tilde{\gamma}(\tau)$ stands in v_u and in $\tilde{\tau}(u)$. Moreover in $\tilde{\tau}(u)$ it is at least the dependence on $\tilde{\gamma}$ in all preceding moments of time. So, the last equation is very complex and one has to suggest some methods of the approximate solution.

16 Approximate solution

When $\tilde{\gamma}$ is really smaller than $\tilde{\gamma}_0$ corresponding to $r = 0$ it is possible to see that some approximations for $\tilde{\gamma}$ produces approximations for evolution.

When the main influence is ensured by the supercritical tail then the condition

$$G_{tail} = const$$

is rather productive.

One can approximately say that in the region $\rho < \rho_b$ the rate of growth is very small.

Another possibility is to use for $du/d\tau$ an approximation which can be integrated analytically. Namely $du/d\tau$ has to be used because for u the boundaries of the nearcritical region and supercritical region will be fixed. For

$$\frac{du}{d\tau} = (1 - u^{-1}) - \tilde{\gamma}u$$

we use the following constructions:

- We give definitions

$$F_1 = (1 - u^{-1})$$

$$F_2 = r$$

$$F_3 = 1 - \tilde{\gamma}u$$

- The first interval will be $[u_2, \infty[$. The value of u_2 is the root of equation

$$F_2 = F_3$$

At the first interval one can approximately write

$$\frac{du}{d\tau} = F_3$$

The last equation can be integrated analytically

- The second interval is $[u_1, u_2]$ where u_1 is the root of equation

$$F_2 = F_1$$

At the second interval one can approximately write

$$\frac{du}{d\tau} = F_2$$

The last equation can be integrated analytically

- The third interval is $[0, u_1]$. At the third interval one can approximately write

$$\frac{du}{d\tau} = F_1$$

The last equation can be integrated analytically

Summarizing one can approximately write

$$\frac{du}{d\tau} = \bar{F}(u, \tilde{\gamma})$$

with an analytical solution. Then we know $\bar{\tau}(u)$ and can write a closed equation on $\tilde{\gamma}$.

This approach will be called as the "regular-regular model".

In the general situation allowing LS asymptotics

$$du/d\tau = F_1 - \tilde{\gamma}u$$

and the procedure remains the same.

Another possibility is the quasistationary approximation. Here $\tilde{\gamma}$ is supposed to be a local constant and the law of growth is integrated

$$\tau(u) = \int \frac{du}{F_1 - \tilde{\gamma}u}$$

Then we know $\tau(u)$ and $\xi(\tau - \tau(u))$ as function of u, τ . Then the balance equation is the closed equation on $\tilde{\gamma}$.

Define as τ_{total} the time of dissolution from the size u_m , where $du/d\tau$ attains maximum, up to zero. It is clear that the necessary condition for the applicability of the quasistationary approximation is

$$\frac{|\tau_{total}(\tilde{\gamma}(\tau)) - \tau_{total}(\tilde{\gamma}(\tau + \tau_{total}(\tilde{\gamma}(\tau))))|}{\tau_{total}(\tilde{\gamma}(\tau))} \ll 1$$

The difference between LS and OK theories symbolizes that at the asymptotics $r = 0$ the quasistationary approximation can be hardly applied at the very end of the process. But it can be fruitful at some earlier periods.

17 Combination of approaches

Here the regular-regular model and the diffusion-regular models of solution were presented. Now it is necessary to decide what model has to be used.

The main object will be the support of spectrum. We shall define the essential support of the spectrum by the following way:

- For G_{total} we define the subintegral function g by

$$G_{total} = \int d\rho g_\rho$$

or

$$G_{total} = \int du g_u$$

- We define the maximum of g and

$$\rho_{max} = \arg(max(g))$$

$$u_{max} = \arg(max(g))$$

- Then we determine the region of support by

$$\int_0^{u_l} du g_u = \delta/2$$

$$\int_{u_r}^\infty du g_u = \delta/2$$

or by

$$\int_0^{\rho_l} d\rho g_\rho = \delta/2$$

$$\int_{\rho_r}^\infty d\rho g_\rho = \delta/2$$

with some small parameter δ .

This region can be also determined by conditions

$$g(u_l) = g(u_r) = \delta g(u_{max})$$

If the essential support belongs to the near-critical region then we have to use the diffusion-regular model. In the opposite situation we have to the regular-regular model.

The impulse regime contains the sequential application of the diffusion-regular model and the regular-regular model. Here the evolution during the period described by the regular-regular model occurs in a very simple manner - the essentially supercritical droplets determine the behavior of the supersaturation. So, there is no need to use the complete formalism of the regular-regular model.

In the regime of adjusted tail one has to use the regular-regular model which can not be simplified.

To see the times when the regular-regular model will be no longer valid it is possible to apply the diffusion operator to the solution obtained in the regular-regular model. When the difference between this solution and the result of the application of diffusion operator will be essential it means that it is necessary to introduce the diffusion corrections.

The presence of diffusion corrections will be very essential at the tail of the size spectrum and namely this tail will govern the evolution later. This tail can be hardly described by the diffusion equation because there is no statistics - only few droplets of big sizes determine the evolution.

Ordinary, the process of nucleation results in existence of several big droplets with stochastic sizes and namely their competition in growth determines the latest stage of the process. The sizes of these droplets are rather arbitrary. So, the kinetics of interaction will be also unstable and arbitrary. This effect forms a matter of a special publication.

Here it is necessary only to add that the number of droplets strongly diminishes in time and to see the impulse regime and later the regime of adjusted tail it is necessary to have a nucleating system of huge sizes.

References

- [1] Lifshitz I.M., Slyozov V.V. The kinetics of precipitation from supersaturated solid solutions - J.Phys.Chem.Solids, 1961, v.19, N 1/2, p.35
- [2] Kukushkin S.A., Osipov A.V. Kinetics of the first order phase transitions at the asymptotic stage, Journal of Experimental and Theoretical Physics, vol. 113, issue 6, p.2193-2208 (1998)

- [3] Kukushkin S., Osipov A, J.Chem.Phys. vol. 107 p 3247-3252 (1997)
- [4] Kuni F.M., Grinin A.P., Kabanov A. S. Kolloidnui journal vol 46, p 440 (1984)
- [5] Kurasov V. General trends of the late period of evolution in the quasichemical model of nucleation, Preprint arXiv.org chemical physics 0607768 (2006)
- [6] Kurasov V. B., Universality in kinetics of the first order phase transitions, Chemistry Research Institute of Sankt-Petersburg State University, St.Peterburg, 1997, 400 p.
- [7] Kurasov V.B., Development of the universality conception in the first order phase transitions, Chemistry Research Institute of Sankt-Petersburg State University, St.Peterburg, 1998, 125 p.